

High-temperature Low End Rheology Modifier Proves Effective in 15% NaCl Water-based Drilling Fluid

Janine Shipman, Meng Lu and Fuchen Liu, CNPC-USA; Richard Bennett, BYK-USA Inc.; Neil Grant, BYK Additives Ltd

Copyright 2023, AADE

This paper was prepared for presentation at the 2023 AADE National Technical Conference and Exhibition held at the Bush Convention Center, Midland, Texas, April 4-5, 2023. This conference is sponsored by the American Association of Drilling Engineers. The information presented in this paper does not reflect any position, claim or endorsement made or implied by the American Association of Drilling Engineers, their officers or members. Questions concerning the content of this paper should be directed to the individual(s) listed as author(s) of this work.

Abstract

Samples of synthetic mineral and a novel polymer were mixed (at a total dosage of 3-4 lb/bbl) into a 15% NaCl water-based drilling fluid. Samples were tested with and without a weighting agent. The highest mud-weight was a 2.0 sg. They were hot-rolled up to 240°C (464°F) and then tested on a baseline (direct indicating rheology) viscometer. Most of these samples were also tested on a high-temperature high-pressure rheometer. Just to see what it did at lower concentrations drilling fluids of 2% NaCl were tested as well. Environmental testing was performed as well.

Samples showed that the combination of the novel polymer and synthetic mineral showed the ideal results with stable and desirable values for the 6-, 3-rpm, 10-sec, and 10-min gel measurements. The mixture was compared to samples with just the synthetic mineral, just the novel polymer, and a blank. The mixture showed to be ideal when the samples endured high temperatures of 240°C. A sample weighted to 2.0 SG was tested to shed light on how the 2 components when added individually appear to have an impact on different criteria. The synthetic mineral appears to keep the immediate 6, 3 rpm numbers in tolerable ranges, while the polymer appears to create an ideal environment to have increased 10-minute gels. Environmental testing results were good.

Introduction

Oil and gas production is no longer focusing on mature and conventional reservoirs. It is now shifting to deeper and hotter wells. Therefore, the demand for drilling fluid additives and systems with higher thermal stability will increase (Shah et al. 2010). When drilling in environmentally sensitive or cost-challenging areas the use of water-based fluids maybe more desirable (Tehrani et al. 2007). Operators have been relying on polymers for several drilling fluid traits, including rheology control, for HPHT applications. They are appealing because of their ability to be environmentally friendly, cost effective, as well as highly effective at high temperatures and with a variety of salt concentrations (Liu et al. 2019). Synthetic minerals can also be used as viscosifiers in drilling fluids for high temperature applications (Neumann B.S. 1962). The focus of this paper is to investigate the synergy in terms of rheology when combining the synthetic minerals and polymers and

observing their tolerance to HPHT conditions and high salinity.

Low End Rheology

Drilling fluids are characterized by several means. Of particular importance is their ability to deform and flow at a variety of applied forces. Optimum behaviors at low flow and shear rates are of particular importance to the fluids' ability to suspend solids (both added and drilled) at static (or near-static) conditions so that when flow begins again, they may continue to move and be removed, if needed, from the drilled hole. The different measurements performed to ascertain the fluids' ability to do this are, the 6-rpm, 3-rpm, 10"-gel, and 10'-gel readings. For this paper these measured values will be the primary focus. (Jachnik 2005). Although the focus is on this, full rheological profiles were measured on all samples (i.e., 600rpm, 300rpm & etc.).

Challenge Parameters

The objective was to design a low-end rheology package for a water-based slurry up to 15% NaCl (with varying specific gravity up to 2.0 SG) and that it should be stable at 240°C (464°F). The material needed to pass an environmental test with the result of $LC_{50} \geq 30,000$ ppm. The testing parameters: 6, 3-rpm, 10-sec, and 10-min gels needed to be > 2 lb/100ft² after being hot-rolled to 240°C/464°F for 16-hours.

Other values, like fluid loss, were not measured. The primary focus was the low-end rheology of the system. It was assumed that when the full system was formulated this value would be evaluated and any products needed to be added would be done at that time.

Materials

The synthetic mineral has been used in several applications across several industries and is typically paired with polymers to enhance its qualities. It is theorized that the synthetic mineral charged particles develop an electrostatic association with the oppositely charged sections of the co-polymer to enhance its capabilities within the fluid (Neumann 1962). See Figure 1 for an illustration of the probable relationship.

The polymer is described as a slightly crosslinked water-soluble copolymer with vinylsulfonate groups. The vinylsulfonate groups are relatively stable to hydrolysis at high temperature. They also are known to have good tolerance to

divalent ions such as Ca^{2+} . The intramolecular crosslinking with diacrylamide will further improve the thermal stability of the polymer. In addition, as an anionic polymer, the vinylsulfonate can have strong interaction with the charged synthetic mineral particles. Five polymers with different molecular weight, degree of crosslinking and molar concentration of sulfonate were used in this study and their structural comparison is summarized in Table 1.

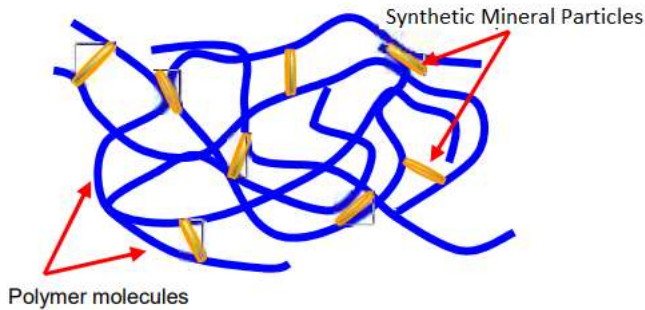


Figure 1: Illustration of Possible Polymer-Synthetic Mineral Relationship

Table 1: Comparison of the polymers

Polymer	Degree of crosslinking	Molar concentration of sulfonate	Molecular weight
P-1	Medium	High	Medium
P-2	None	High	Medium
P-3	Medium	Medium	Low
P-4	Low	Medium	Medium
P-5	Medium	High	Low

Experimental Evaluation

Lab Test Descriptions

Water based slurries were made with the following formulations:

Table 2: Unweighted 15% NaCl Slurry

Material	Amount Unit
Water-DI	350.0 mL
NaCl	52.5 grams
Attapulgate	20.0 grams
NaOH	1.0 grams (~pH 9.5)
Na_2SO_3	2.0 grams
Defoamer	As needed

Attapulgate (API grade) was used as it was readily available in the laboratory and it was felt, that in comparison to sepiolite, it would affect the low-end rheologies less (and at high temperatures).

Table 3: Weighted Slurry

Material	Amount Unit
Water-DI	233.0-mL
Barite	To 2.0 SG 450-500 grams
NaOH	1.0 gram (~9.5 pH)
NaCl	41.3 grams
Na_2SO_3	2.0 grams

All slurries had the polymer (P) mixed at a dosage of 1.0 lb/bbl and the synthetic mineral (SM) at 2.0 lb/bbl (unless stated otherwise).

Slurries were mixed in accordance with their additives and a hot-roll was performed at 120°F to ensure full integration of all components. Rheologies were usually measured after the 120°F hot-roll on the standard direct indicating viscosity rheometer. Samples were remixed, pH adjusted, if need be, oxygen scavenger was added, and slurry was placed in a pressurized (550 psi) hot-roll cell to be hot-rolled at 464°F for 16 hours. These samples were measured by the standard direct indicating viscosity rheometer (per API recommended practices) and the high-pressure high temperature (HPHT) rheometer. The HPHT rheometer testing parameters were set to:

Table 4: HPHT Rheometer Parameters

Parameter	Value
Temperature	200°C and then 240°C (464°F)
Pressure	2000 psi

Lab Test Results

Initially, different synthetic mineral sets were tested in slurries with different concentrations of NaCl to see how it responded to salt solutions by themselves. The sample slurries used API-grade bentonite or attapulgate as the primary gellant. The 2-5% NaCl brine slurries contained API bentonite, whereas, 10-15% NaCl brine slurries were formulated with attapulgate. Samples were hot-rolled at 120°F (50°C) for 16 hours before testing on a standard direct indicating viscosity rheometer. Their (including a blank with no synthetic mineral) results are summarized in Figures 2-7.

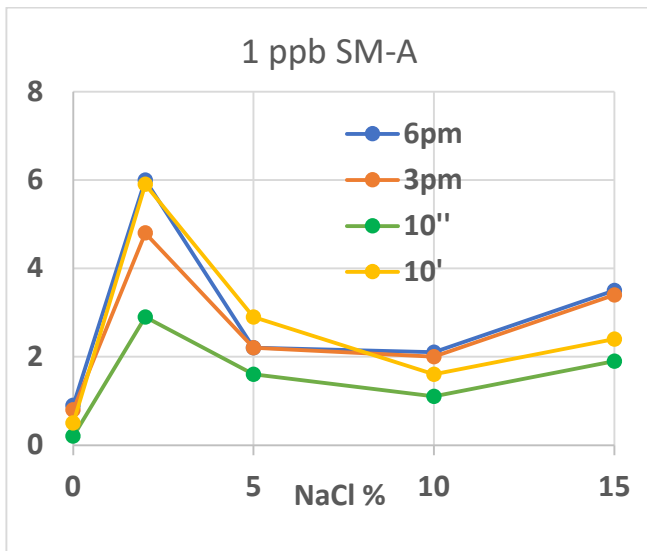


Figure 2-Testing Synthetic Mineral A in Various Salt Contents

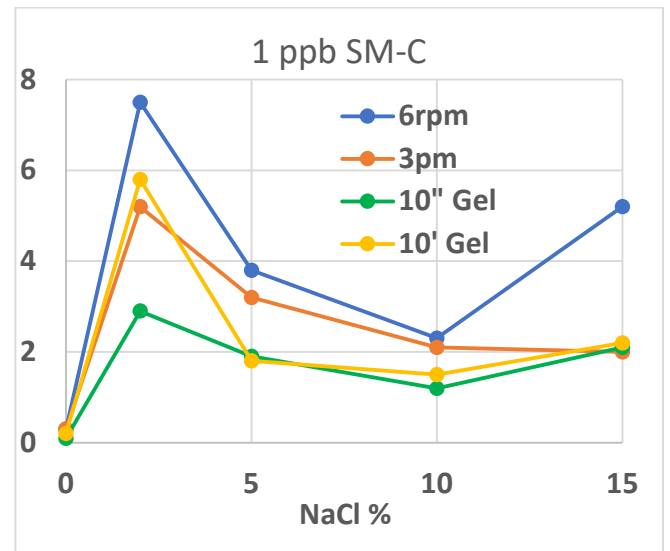


Figure 4-Testing Synthetic Mineral C in Various Salt Contents

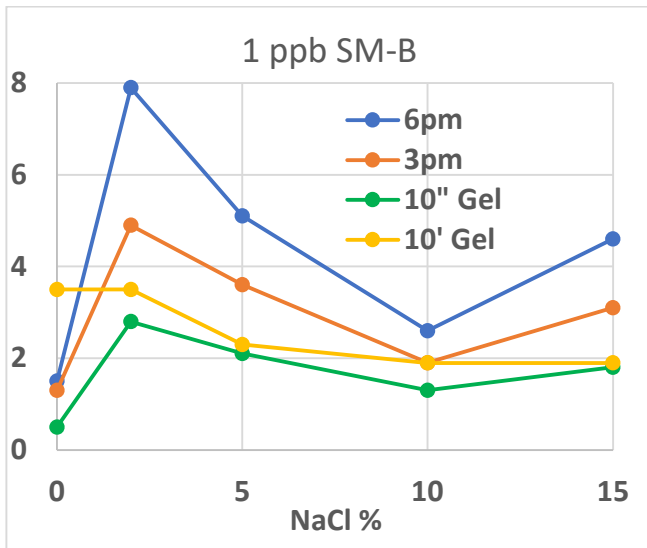


Figure 3-Testing Synthetic Mineral B in Various Salt Contents

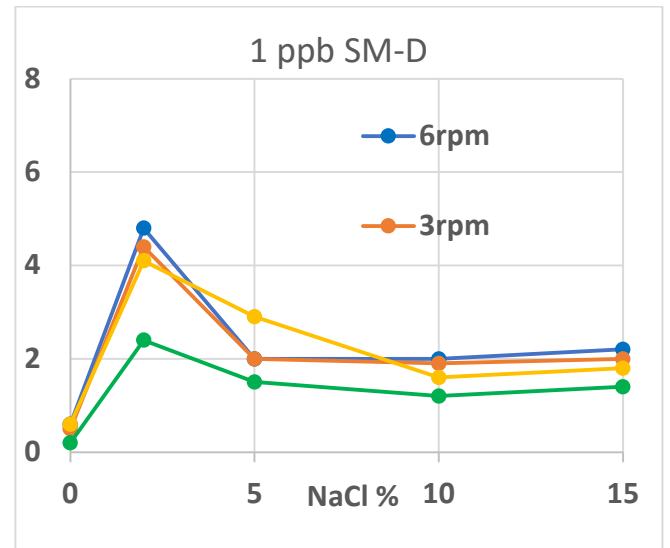


Figure 5-Testing Synthetic Mineral D in Various Salt Contents

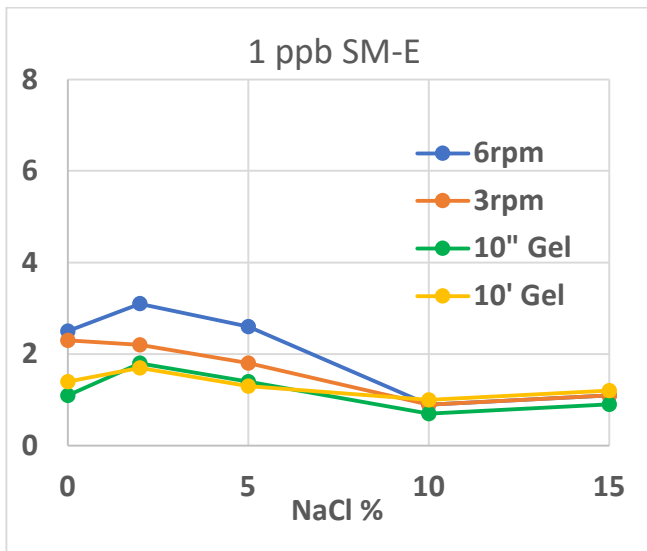


Figure 6-Testing Synthetic Mineral E in Various Salt Contents

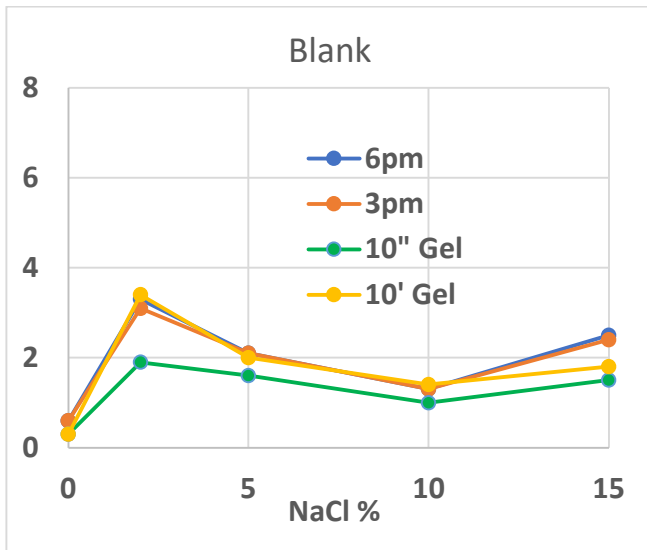


Figure 7-Testing a Blank Slurry in Various Salt Contents

Based on the data Synthetic Mineral-B had the best rheological behavior because, when compared with the others, the readings were better across all salt concentrations. This is bearing in mind, that when the salt concentrations were 0-5% salt the samples had bentonite to assist in suspension. The samples with 10-15% had attapulgite.

SM-B was chosen to pair up with several different polymers. Tested at two temperatures (200°C/392°F (Figure 8) and 240°C/464°F (Figure 9)), respectively.

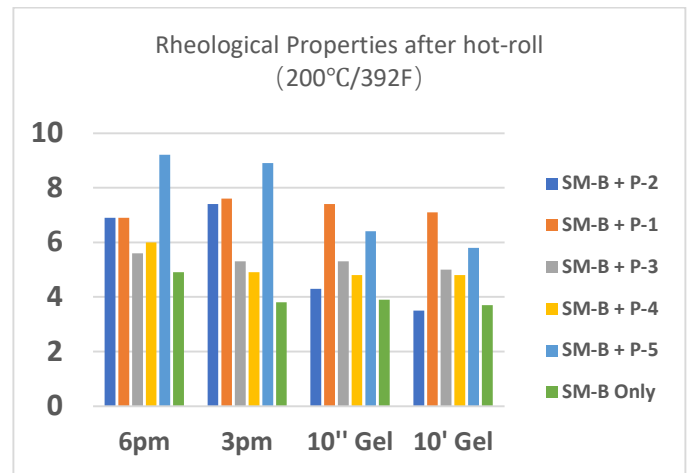


Figure 8-Testing Synthetic Mineral B with various Polymers at 15% NaCl Salt in 200°C

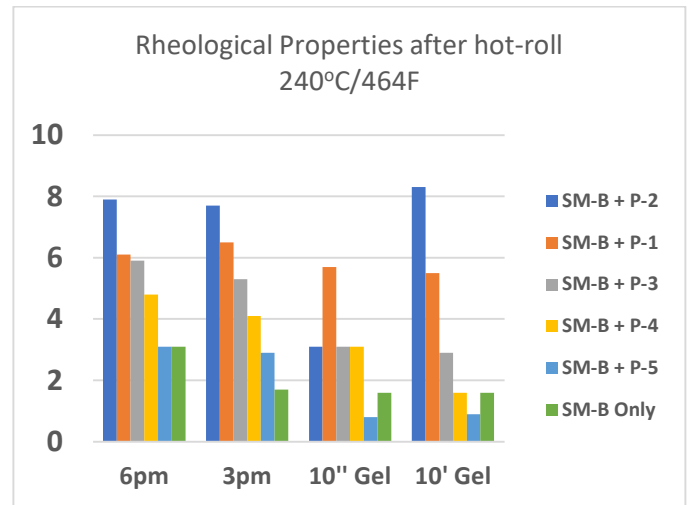


Figure 9-Testing Synthetic Mineral B with various Polymers in 15% NaCl Salt at 240°C

When paired with SM-B, and hot-rolled at 200°C, all the polymers showed good thermal stability and tolerance to high salinity. However, after the samples were hot rolled at 240°C, polymers P-1 and P-2, polymers with high ionic concentration and higher molecular weight, showed better stability. The intermolecular crosslinking in P-2 could further extend the polymer's stability. With the difference in how products performed between 200°C/392°F vs 240°C/464°F it was decided to observe polymer P-2 with three of the synthetic minerals of interest (again at 200°C (Figure 10) and 240°C (Figure 11)).

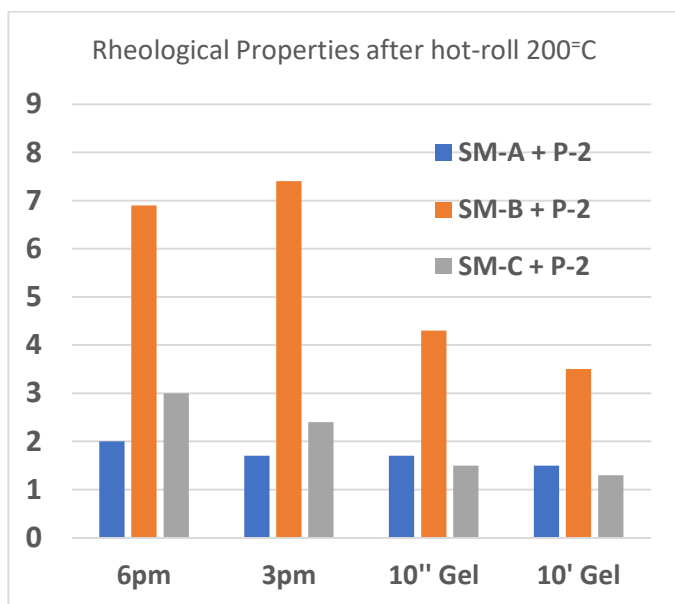


Figure 10-Testing Synthetic Minerals with Polymer-2 at 15% NaCl Salt in 200°C

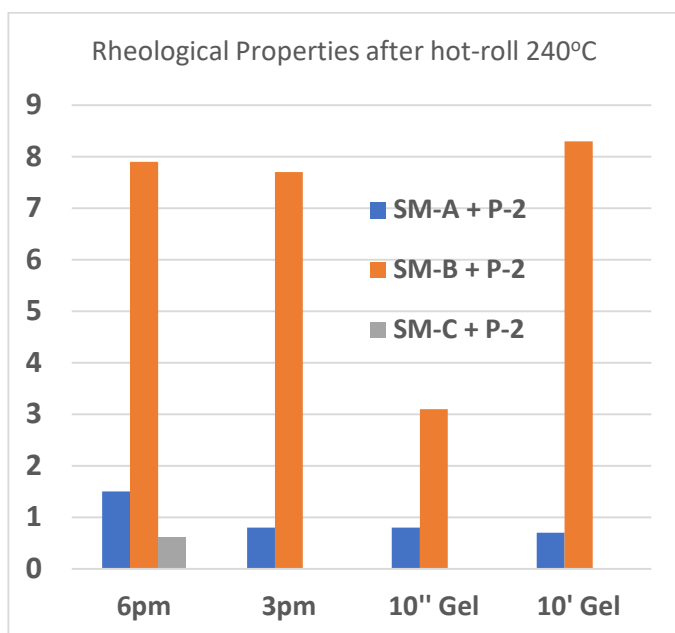


Figure 11-Testing Synthetic Minerals with Polymer-2 in 15% NaCl Salt at 240°C

It was confirmed that the best combination for this temperature range was Polymer-2 and Synthetic Mineral-B. It appeared that the combination showed strong interaction between SM-B and P-2. They provided optimized rheologies at low shear rates. It should be noted that if values were too high in a finalized fluid formulation the application dosage of the combined product could be reduced.

HPHT Rheometer Testing

Samples were run on the high temperature high pressure rheometer to get an idea of their downhole performance (Table

5-7).

Table 5-15% NaCl Unweighted

Temp (°F)	Temp (°C)	Pressure (psi)	Speed (rpm)	lb/100ft ²
403	206	2228	6	14.0
401	205	2041	3	14.1
396	202	2086	10"Gel	11.0
402	206	2050	10'Gel	13.3
475	246	2292	6	13.6
473	245	1997	3	13.6
468	242	1966	10"Gel	3.8
474	246	2016	10'Gel	3.5

Table 6-15% NaCl 2.0 SG

Temp °F	Temp (°C)	Pressure (psi)	Speed (rpm)	lb/100ft ²
393	201	2075	6	7.8
396	202	2005	3	5.2
395	202	2120	10" Gel	5.5
401	205	1971	10' Gel	8.7
458	237	2138	6	5.8
461	238	2026	3	6.5
465	241	2095	10" Gel	5.3
469	243	1980	10' Gel	8.7

Table 7-15% Blank Unweighted for Comparison

Temp (°F)	Temp (°C)	Pressure (psi)	Speed (rpm)	lb/100ft ²
392	200	2087	6	2.0
395	202	2059	3	1.4
395	202	2030	10"Gel	1.4
400	204	2078	10'Gel	1.3
462	239	2062	6	1.1
466	241	2032	3	0.0
469	243	2063	10"Gel	0.0
470	243	2061	10'Gel	0.0

When tested in high pressure-high temperature conditions one can see how well the products perform at 15% NaCl over an array of specific gravities. At low mud weight, attapulgite was used together with P-2 and SM-B to provide good rheology as shown in Table 5. With increased mud weight, the increased solids increase the overall viscosity. The polymer and synthetic mineral continued to support the low end rheology performance (Table 6). For comparison, without the polymer and synthetic

mineral, attapulgite alone could not perform at temperature over 200°C/392°F (Table 7).

Observations of separate components

Slurries were mixed as stated in Table 2, with the exception that one sample had 1.0 lb/bbl P-2 only and the other had 2.0 SM-B only. When tested on the direct indicating viscosity rheometer (at 50°C) separated components (tested after 240°C/464°F) ‘P-2-only’ the 10”, 10’ Gels could be seen as too high. SM-B appears to act acceptably on the baseline rheometer (Table 8):

Table 8: Unweighted 15% NaCl Components Independently Measured on Baseline Rheometer

Individual components	After 120		After 464°F	
	1 lb/bbl P-2		2 lb/bbl SM-B	
	Polymer Only		Synthetic Mineral Only	
600 rpm	22.1	6.6	16.5	11.6
300 rpm	19.2	4.6	14.0	9.2
200 rpm	17.7	4.3	13.0	8.6
100 rpm	15.9	3.1	11.8	7.8
6 rpm	11.8	3.4	8.5	8.7
3 rpm	7.3	1.5	8.2	4.7
PV	2.8	1.9	2.5	2.2
YP	16.6	2.8	11.7	7.2
Gels 10"	5.5	5.5	6.6	6.8
Gels 10'	6.6	10.6	6.8	7.0

When tested on the HTHP rheometer the component’s functionality may be better speculated.

The SM-B by itself, in an unweighted slurry, appears not to be effective at this temperature and salt content (Table 9). But when seen in a weighted slurry SM-B acts more independently improving the low-end rheology (Table 10):

Table 9-HPHT Testing of SM-B by itself Unweighted at 240°C/464°F

Temp(°F)	Temp(°C)	Pressure(psi)	Speed (rpm)	lb/100ft ²
462	239	2150	6	3.1
464	240	2021	3	1.7
464	240	2021	10 sec Gel	1.6
473	245	2013	10 min Gel	1.6

Table 10-HPHT Testing of SM-B by itself in 2.0 SG Fluid at 240°C/464°F

Temp(°F)	Temp(°C)	Pressure(psi)	Speed (rpm)	lb/100ft ²
457	236	2000	6	3.6
462	239	2019	3	2.6
468	242	2044	10 sec Gel	1.1
467	242	2051	10 min Gel	9.5

The P-2 by itself appears to be acceptable unweighted (Table 11):

Table 11-HPHT Testing of P-2 at 240°C/464°F

Temp (°F)	Temp (°C)	Pressure (psi)	Speed (rpm)	lb/100ft ²
475	246	2057	6	13.4
473	245	2247	3	13.3
468	242	2014	10sec Gel	3.8
473	245	2276	10min Gel	4.4

However, when weighted the sample with just P-2 lost all favorable low-end rheological capabilities. The Weighted P-2 sample was not tested on the HPHT rheometer due to barite settling.

Observations of combined components

Table 12: Unweighted 15% NaCl P-2+SM-B-Rep on HTHP Rheometer

Temp (°C)	Temp (°F)	Pressure (psi)	Speed (rpm)	lb/100ft ²
235	455	2040	600	7.8
234	453	1991	300	7.4
236	456	2035	200	7.3
237	459	2127	100	7.3
239	462	2060	6	5.9
240	464	1975	3	5.3
242	467	2011	10" Gel	2.9
244	472	1949	10' Gel	3.4
PV	0.5		YP	6.9

Table 13: Weighted 15% NaCl Combined on HTHP Rheometer

Temp (°C)	Temp (°F)	Pressure (psi)	Speed (rpm)	Lb/100ft ²
237	458	2068	600	18.5
234	454	2058	300	13.2
235	455	1978	200	10.1
236	456	2107	100	8.4
237	458	2138	6	5.8
238	461	2026	3	6.5
241	465	2095	10"Gel	5.3
243	469	1980	10'Gel	8.7
PV	5.4		YP	7.8

As shown in Table 12, when P-2 was combined with SM-B, the low-end rheology of the slurry has a better profile indicating the possible interaction between the polymer and synthetic minerals may provide a synergetic effect. Looking at both Tables 12 & 13, the whole rheological profile indicates that at any density the viscosicity, at high shear, is not effected to a large degree. In other words, the combination of the chosen polymer and synthetic mineral is mainly effecting the low-end rheologies at low shear rates.

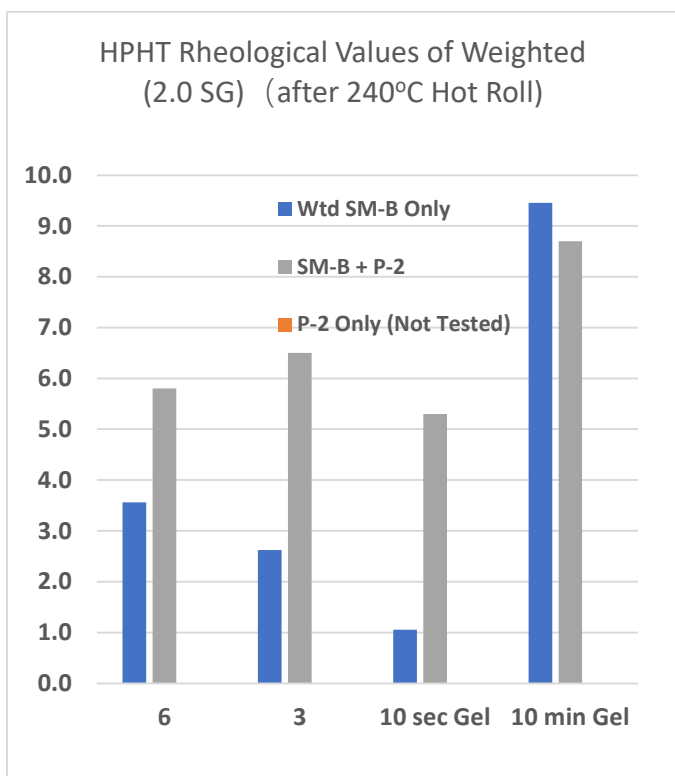


Figure 12-Testing Components Individually on HPHT Rheometer – 2.0 SG Slurry with 15% NaCl Salt at 240°C

Environmental Testing

Several aliquots of the unweighted slurry were combined and sent off for environmental testing. This test was described as a 96-hour acute *Mysidopsis bahia* (mysid shrimp) toxicity test at 20°C (Test method EPA-821-R-11-004-1619.0 92011). The estimated median lethal concentration (LC50) of the sample was >3% SPP (30,000 ppm). Although the full system would need to be tested, the products by themselves, if used offshore, should be able to be discharged.

Conclusions

The selected synthetic mineral and polymer worked well together to ensure the low-end rheologies stayed at or above minimum expectations for weighted and unweighted water-based drilling fluids at high temperature with tolerance of high salinity. These products together offer an environmentally friendly approach to treating a water-based drilling fluid's ability to carry, lift and suspend solids during low-shear drilling operations at high salt, temperatures, and pressures. Next steps are to see how it does with divalent cations and to see if we can further improve those components.

Acknowledgments

The authors would like to thank CNPC-USA and BYK for allowing us to publish this information. Special appreciation goes towards Songbing Yan and Weibin Zha for their contributions and support during the project. We would also like to express our gratitude to Brett Cramer. We would also like to thank all employees of the organizations and our families for their encouragement and support.

Nomenclature

HPHT = High Pressure High Temperature

LC50 = Median Lethal Concentration

P = Polymer

ppb = pound per barrel

SM = Synthetic Mineral

SPP = Suspended Particulate Phase

References

- Heier, K., & Kayser, C. 2008 "Vinylsulfonate-vinylamide copolymers and cross-linkable modifications thereof-Up-to-date chemicals for HTHP drilling, cementing and completion fluids." AADE Fluids Conference and Exhibition, Houston, April 8-9, 2008. Available [here](#).
- Jachnik, R.: "Drilling Fluid Thixotropy & Relevance". Annual Transactions of the Nordic Rheology Society v. 13, 2005.
- Liu, X., Gao, Y., Hou, W., Ma, Y., & Zhang, Y. 2019 "Non-Toxic High Temperature Polymer Drilling Fluid Significantly Improving Marine Environmental Acceptability and Reducing Cost for Offshore Drilling" International Petroleum Technology Conference, Beijing, China, 26-28 March 2019. <https://doi.org/10.2523/IPTC-19425-MS>
- Neumann B.S. "Improvements in or relating to Synthetic clay-

- like Minerals.” UK Patent GB1054111 Filed 26/06/1962.
5. Neumann B.S. “Clays” UK Patent GB1213122 Filed 12/09/1966
 6. Patel, A., Stamatakis, E., & Young S. 2007. “High Performance Water-Based Drilling Mud and Method of Use”. US Pat No. 7,514,389 filed Sept. 3, 2003 now US Pat. 7,192,907, Issued 03/20/2007.
 7. Shafran, K., Jeans, C., Kemp, S., & Murphy, K. 2020. “Dr Barbara S. Neumann: clay scientist and industrial pioneer; creator of Laponite”. *Clay Minerals*, 55 (2020): 256-260. [doi:10.1180/clm.2020.35](https://doi.org/10.1180/clm.2020.35)
 8. Shah, S.N., Shanker, N.H., and Ogugbue, C.C.. 2010. “Future Challenges of Drilling Fluids and their Rheological Measurements.” AADE-10-DF-HO-41, AADE Fluids Conference and Exhibition, Houston, April 6-7, 2010. Available [here](#).
 9. Tehrani, M.S., and Popplestone, A. 2007. “Water-Based Drilling Fluid for HP/HT Applications”, SPE International Symposium on Oilfield Chemistry, Houston, 28 Feb-2 March, 2007. SPE 105485-MS. <https://doi.org/10.2118/105485-MS>
 10. Tehrani A., Gerrard, D., Young, S., & Fernandez, J. 2009. “Environmentally Friendly Water-Based Fluid for HPHT Drilling” SPE International Symposium on Oilfield Chemistry, The Woodlands, 20-22 April 2009. SPE 121783-MS. <https://doi.org/10.2118/121783-MS>
 11. Vipulanandan, C., & Mohammed, A. “Smart Cement Modified with Laponite for Real Time Monitoring of Oil Well Cementing Applications” AADE National Technical Conference and Exhibition, Houston, April 11-12, 2017. Available [here](#).